

Volatility and Performance Studies of Phosphate Ester Boundary Additives With a Synthetic Hydrocarbon Lubricant

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13. ABSTRACT (<i>Maximum 200 words</i>) <p>The development of advanced synthetic hydrocarbon oils having very low vapor pressures for spacecraft applications has both enabled the use of boundary additives developed for mineral oils and amplified the shortcomings of these additives. For example, tricresylphosphate (TCP) is widely used in the spacecraft industry as a boundary additive to limit wear, but the vapor pressure of TCP is several orders of magnitude higher than that of Pennzane, a synthetic hydrocarbon oil. In this report, we document the volatility of TCP and higher molecular weight commercial phosphate esters with experimental evaporation studies and supercritical fluid chromatography (SFC) analyses. The performance of these additives under accelerated screening tests is also presented. The test results show that the least volatile additive provides the greatest endurance in these vacuum wear tests, but the performance of the four different additives does not strictly follow this trend. The results indicate that the short-term tests may be too severe to distinguish additive performance based solely on volatility. Further test results demonstrate that the effect of formulating the oil with the additive is much greater than merely pre-treating the bearing components with TCP, and that the protective film developed early in the wear life with a formulated oil provides significant protection.</p>				
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1. Introduction

The performance of liquid-lubricated spacecraft mechanisms that operate under boundary conditions (insufficient lubricant film thickness to prevent metal-to-metal contact) is strongly dependent on the performance of boundary additives (anti-wear, friction modifying) formulated with the lubricant. The lack of effective boundary additives for perfluoropolyalkylether (PFPE) lubricants has prevented the exploitation of the extraordinary properties of these fluids (e.g., very low vapor pressure, low pour point) in many spacecraft applications. In recent years, synthetic hydrocarbons with very low vapor pressures, comparable to PFPEs, have been developed. Since these oils are hydrocarbons, additives developed for mineral oils can be formulated into these advanced basestocks, improving their boundary lubrication performance relative to PFPEs. The multiply alkylated cyclopentane (MAC) lubricant Pennzane 2000 has drawn considerable interest in the spacecraft community. Pennzane has many extraordinary properties, including low vapor pressure ($<1 \times 10^{-11}$ Torr at room temperature), excellent viscosity properties,¹ and documented lower torque than equivalent viscosity mineral oils in bearing applications.² The choice of the best additive to complement the excellent properties of the Pennzane basestock for a particular spacecraft application must be determined through testing, and this report documents the performance of several organo-phosphate ester additives formulated with Pennzane in a lubricant screening test fixture.

Two different lubricant additives are currently being formulated with Pennzane for spacecraft mechanisms. Lead naphthenate (Pbnp) is an extreme pressure additive with a low vapor pressure of less than 1×10^{-9} Torr at room temperature.³ The problems with Pbnp are associated with its lead content and its protective mechanism; the Pbnp molecule decomposes in mechanical contacts,⁴ leaving behind an anti-wear film containing lead and carbon that can be quite thick.⁵ The generation of this thick and often patchy film could cause torque noise problems for very sensitive applications.⁶ The other commonly used additives are phosphate esters such as tricresyl phosphate (TCP). TCP has been shown to be an effective boundary additive that does not form thick films of carbonaceous residue. However, TCP has a much higher vapor pressure than either Pbnp or Pennzane, in the range of 10^{-7} to 10^{-8} Torr at room temperature.⁷ The high vapor pressure causes TCP to be lost rather rapidly in the vacuum of space and limits the benefits of the low vapor pressure of the Pennzane fluid in decreasing spacecraft self-contamination and extending the life of the mechanical device. Analogs to TCP, with different organic chains appended to the phenyl rings, are also commercially available as lubricant additives. Some of these materials have higher molecular weights than TCP, and hence lower vapor pressures, which should be advantageous in vacuum lubrication, provided that the varying chain lengths do not interfere with the function of the additive. This report provides comparative studies of the volatility and performance of some of these commercial additives (which are blends of several organic phosphate esters) in Pennzane to determine which currently available materials perform best with the synthetic oil and to guide the future development of more effective additives.

This report presents results from volatility studies and wear-life screening tests. The screening tests were conducted in vacuum using Pennzane with four commercially available phosphate esters, and test components made from 52100 and 4118 carburized steels. In addition to the

work reported here, analyses of the residual gas atmosphere during tests and the lubricant and wear surfaces after tests were performed and will be reported separately. In this work, the main emphasis is placed on identifying which esters formulated with Pennzane were most effective in increasing the endurance of the bearing test, which esters exhibited the lowest volatility, and whether the performance was directly related to ester additive volatility.

2. Experimental

2.1 MAC Base Oil and Phosphate Ester Additives

The MAC oil used in this work is Pennzane 2000, originally developed by Pennzoil and now sold as Rheolube 2000 by Wm. F. Nye of New Bedford, MA. Table 1 identifies the four triarylphosphate additives procured for testing in addition to a brief chemical description, vendor, and some relevant impurity concentrations. The additives were obtained from two different commercial sources—Nye and FMC Corp. of Philadelphia, PA. Of the four phosphate esters, two are commonly referred to as “natural” esters and the other two as “synthetic” esters. The natural esters are produced from the raw materials cresol and xylenol, which derive from petroleum oils and coal tars, while the synthetic esters are produced from a mixture of phenyl and alkyl substituted phenols. The synthetic esters possess numerous advantages over the natural esters in areas of lower production cost, reduced toxicity, and flexibility in tailoring the product to a specific end use. The synthetic esters used in this report are actually blends of mono-, di-, and tri-*t*-butylphenyl phosphate esters in addition to triphenylphosphate (TPP)—see the footnotes for Table 1. The two natural esters are nominally tricresyl phosphate (TCP) and trixylyl phosphate (TXP). It is noteworthy that the desired value for acidity (the ASTM acid number) of these materials is given as < 0.2 mg KOH/g.⁷ While this value is variable among the materials studied in these tests, all of the esters are reported to meet this specification.

2.2 Evaporation Measurements

Fluid evaporation measurements were performed in a turbomolecular-pumped vacuum chamber with a base pressure of 3×10^{-5} Pa (2×10^{-7} Torr). The chamber housed an aluminum heating plate with 16 cavities, each of which could accept a small cup (10 mm inner diameter \times 4 mm deep). The heater cavity was deep enough so that the top of the cup was flush with the heater surface to minimize any temperature gradients in the sample. A low outgassing, flexible heater

Table 1. Phosphate Ester Additives

Sample ID	Ester Type	Vendor	Acid ^d (mg KOH/g)	Total Halogen ^e (ppm)
TCP	natural ^a	FMC	0.09	ND ^f
TXP	natural ^b	Nye	0.17	<10
620B	synthetic ^c	FMC	0.05	<10
8478	synthetic ^c	Nye	0.09	<10

(a) tricresylphosphate including various isomers

(b) trixylylphosphate including various isomers

(c) four component mixtures

(i) triphenylphosphate

(ii) *t*-butylphenyldiphenyl phosphate

(iii) di-*t*-butylphenylphenyl phosphate

(iv) tri-*t*-butylphenylphosphate

(d) ASTM D974

(e) ASTM D808

(f) No determination

with a programmable temperature controller was attached to the back of the heating plate. Three thermocouples were positioned at various locations on the aluminum heating plate to ensure uniform heating. The controller maintained the temperature to within $\pm 2^{\circ}\text{C}$. The volatilities of three neat additives (TXP and the two synthetics) and the MAC oil were measured in triplicate to ensure statistical confidence.

To perform the evaporation studies, approximately 0.05 g of the desired additive or oil was added to each cup. After the lubricant-containing cups were placed into the vacuum chamber, and the chamber was evacuated, the samples were heated to a specific temperature for a predetermined period. The chamber was pumped continuously during the heating process. After each run, the samples were allowed to cool to room temperature; the cups were removed from the vacuum chamber and weighed to the nearest 0.0001 g. The samples were placed back into the chamber, and another temperature/time profile was performed.

The composition of the additives and the Pennzane basestock was examined with supercritical fluid chromatography (SFC). SFC is an analytical technique that separates the components of a mixture based on their solubilities in supercritical CO_2 , which is related to their molecular weight and hence their volatility. The SFC results will be compared to the evaporation results and bearing wear lives to evaluate the performance of the additives. The instrument used for these analyses was a Dionex Series 600 SFC.

2.3 Bearing Test Fixture

The bearing test fixture has been described in detail elsewhere,⁶ but a brief description follows. The test articles consist of one grooved thrust bearing race, a ball set in a steel ribbon retainer, and a flat counterface obtained by polishing the back side of the second bearing race. A controlled amount of misalignment is introduced by mounting the grooved upper race slightly off-center from the rotating flat counterface to increase the amount of ball skidding. The combination of operating on a flat surface and deliberate misalignment leads to a higher Hertzian stress and greater sliding than occurs on a properly aligned grooved raceway. These conditions create more severe stress on the lubricant/additive by forcing metal-to-metal contact, resulting in high temperatures and exposed reactive surface sites. Furthermore, the system was designed without any restrictions to hinder the movement of the lubricant. This ensured that the test was run under conditions where only minimal amounts of oil remained in the contact region. In short, the bearings were operating under severe boundary lubrication conditions.

All tests were run in a turbomolecular-pumped vacuum chamber with a base pressure of $5.3 \times 10^{-7} \text{ Pa}$ ($4 \times 10^{-9} \text{ Torr}$). With lubricants present, the pressure increased to the range of $4 \times 10^{-6} \text{ Pa}$ to $2 \times 10^{-5} \text{ Pa}$ (3×10^{-8} to $1.5 \times 10^{-7} \text{ Torr}$). After lubrication, the bearing was placed in the wear test fixture and loaded to $\sim 214 \text{ N}$ (48 lb). The load created a peak Hertzian contact stress of approximately 1.7 GPa (250 ksi). Prior to full-speed testing, a brief run-in period was initiated. This consisted of ~ 10 min at 600 rpm, followed by ~ 4 min at 1200 rpm, and finally full speed at 1800 rpm until the test failed due to high torque. The failure criterion was a torque increase of three times the nominal operating value. Following the wear test the bearing was removed and stored in a nitrogen-flow desiccator for future analysis.

The reaction torque of the test bearing was measured by an inductive proximity sensor that detected the movement of the upper housing with respect to the lower housing. A set of aluminum flexures connects the two housings. An automatic shutoff switch prevented catastrophic failure of the bearing and test fixture by disabling the motor when the torque became too high. The test fixture did not have an active cooler, therefore the temperature during testing typically reached 70°C to 90°C before equilibrium was established.

2.4 Bearing Description and Preparation

The thrust bearing raceways used in the test were made from carburized AISI 4118 steel and have a raceway diameter of 22.86 mm (0.90 in.). One race from each bearing pair was polished to a 0.25 µm finish on the flat reverse face to serve as the flat counterface. The 12 balls were produced from 52100 steel and have a diameter of 4.75 mm (0.187 in.). The bearings were prepared for testing by cleaning with three consecutive heptane rinses, the first two rinses being aggressively performed in an ultrasonic cleaner. In some instances, the bearings were pretreated by immersing the entire bearing in a TCP bath for 3 days at ~110°C under a nitrogen flow prior to lubricant application. Following the pretreatment, the bearings were cleaned in the manner described above. Subsequent to the cleaning, the bearing parts were immediately dried in nitrogen followed by application of 30 µL of lubricant. The lubricant was applied as evenly as possible among the balls, and the bearing was rotated by hand for approximately 30 s to distribute the lubricant evenly throughout the contact regions of the bearing.

2.5 Tested Lubricant Formulations

Nine different lubricant test conditions were used. As shown in Table 2, two test conditions (A and B) used only neat compounds (TCP or Pennzane), five test conditions were used to study the various additive formulations (C through G), and the final three conditions investigated the effects of pretreatment of the metal parts with the additive (H, I, and J). Four of the lubricant packages

Table 2. Lubricant Formulations Used in the Eccentric Bearing Tests

Test Condition	Base Oil	Additive	Pretreatment	# of Tests
A	NONE	FMC TCP	NO	1
B	YES	None	NO	4
C	YES	Yes ^a	NO	4
D	YES	Nye TXP	NO	7
E	YES	FMC TCP	NO	12
F	YES	Nye 8478	NO	11
G	YES	FMC 620B	NO	8
H	YES	None	TCP	3
I	YES	TXP, 620B ^b	TCP	3
J	YES	TXP, none ^c	NO	1

- (a) Condition "C" is the commercially available product Rheolube 2001 from Nye. The phosphate additive and concentration are proprietary.
- (b) In some instances the Nye TXP was used; in others the FMC 620B was used.
- (c) Bearings were run for 180,000 revolutions with the oil formulated with TXP, then were cleaned and relubricated with neat Pennzane oil and run to failure.

(D through G) were formulated in our laboratory with an ester concentration of 1% v/v in the Pennzane oil. The commercial ester/oil formulation Rheolube 2001 from Nye was also tested. All of the pretreatments were performed with the FMC TCP.

3. Results

3.1 SFC and Evaporation Measurements

The SFC traces for the four additives are provided in Figure 1. This technique separates components of a mixture based on their solubility in supercritical CO₂, which is related to the size of chemically similar molecules. The more soluble species (lower molecular weight) exit the column at shorter retention times. The two natural esters are shown near the top of Figure 1, and the traces reveal broad bands with some superimposed structure. These traces show that both the TCP and TXP additives are composed of many similar compounds (isomers of the structures) and have approximately the same solubility in the supercritical fluid, based on the similar retention times (7.8 to 8.4 min for TCP, 7.8 to 8.7 min for TXP). The TXP trace shows material at longer retention times than the TCP mixture, which is consistent with the slightly higher molecular weight arising from the additional methyl group on the phenyl rings of TXP.

Both of the synthetic esters are purported to be mixtures of mono-, di-, and tri-t-butylphenyl esters along with triphenylphosphate (see Table 1). The Nye 8478 SFC trace has four predominant features that can be associated with these species. The shortest retention time species is the

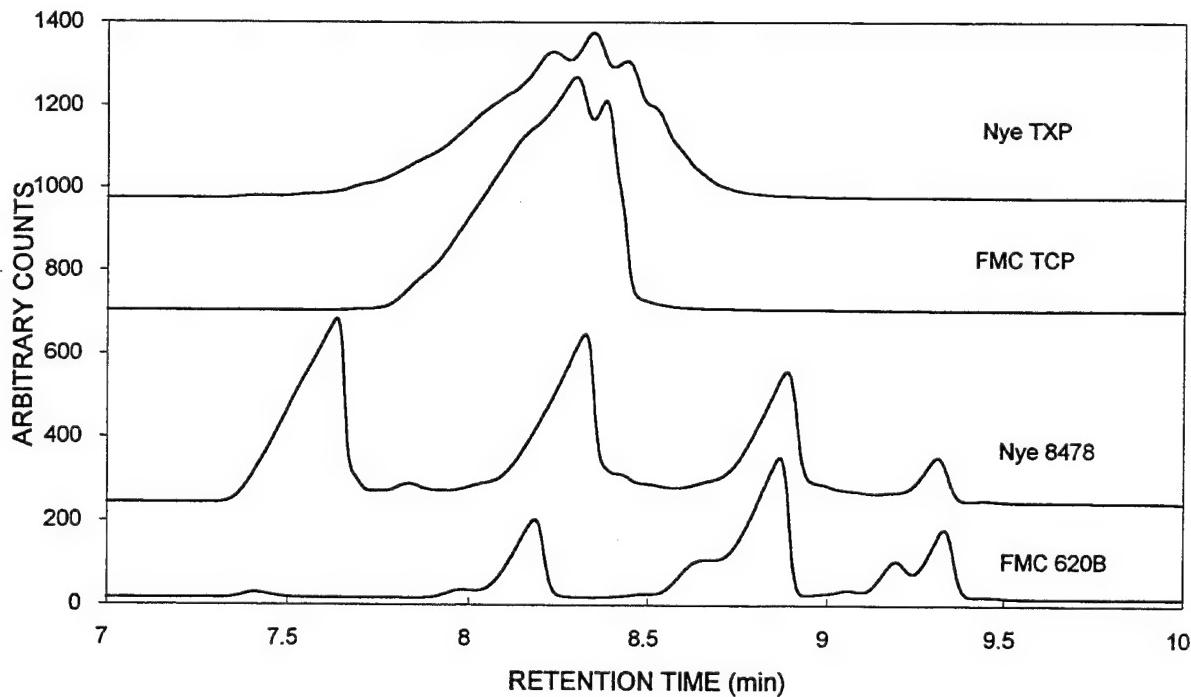


Figure 1. SFC analysis results for the four commercial lubricant additives studied in this work. The name of the additive is supplied on the right side of each trace.

triphenylphosphate, while the remaining species are the t-butylphenyl substituted compounds, with the tri-t-butylphenyl phosphate at the longest retention time. The FMC 620B SFC also reveals several components, but while there are similarities between the two synthetics, there are some obvious differences. First, the largest contributor to the Nye additive is the tri-phenylphosphate, while the FMC product has very little of this volatile component. Second, the predominant component of the FMC 620B is the di-t-butylphenyl compound, providing additional evidence that this additive mixture has a greater amount of high molecular weight species than the Nye mixture. And third, the features in the FMC mixture appear to be doublets, indicating that there are other compounds present in the mixture that are closely related to the predominant components of the mixtures. It is not clear from these data what these additional compounds are.

For comparison, the SFC analysis of neat Pennzane 2000 is provided in Figure 2. The SFC trace was obtained with the same conditions as the additive mixtures, and provides an estimate of the relative volatility of the base oil to the additives. The Pennzane fluid used for spacecraft applications is nominally a mixture of two distinct molecular species, with the predominant species being tri-octyldodecylcyclopentane, and the second species being the smaller di-octyldodecylcyclopentane. The SFC analysis clearly indicates that more than two species are present, but the large feature near 13.6 min retention time must be assigned as the tri-substituted cyclopentane. This would require that the largest peak at shorter retention time (11.5 min) be assigned as the di-substituted cyclopentane. The small features located between 11 and 11.5 min and 12–13 min are likely stereoisomers of the molecules, which contain several chiral centers. The feature at approximately 14.5 min may also be an isomer, but cannot be identified without further analyses. Although the Pennzane molecules are strictly hydrocarbons, and their retention

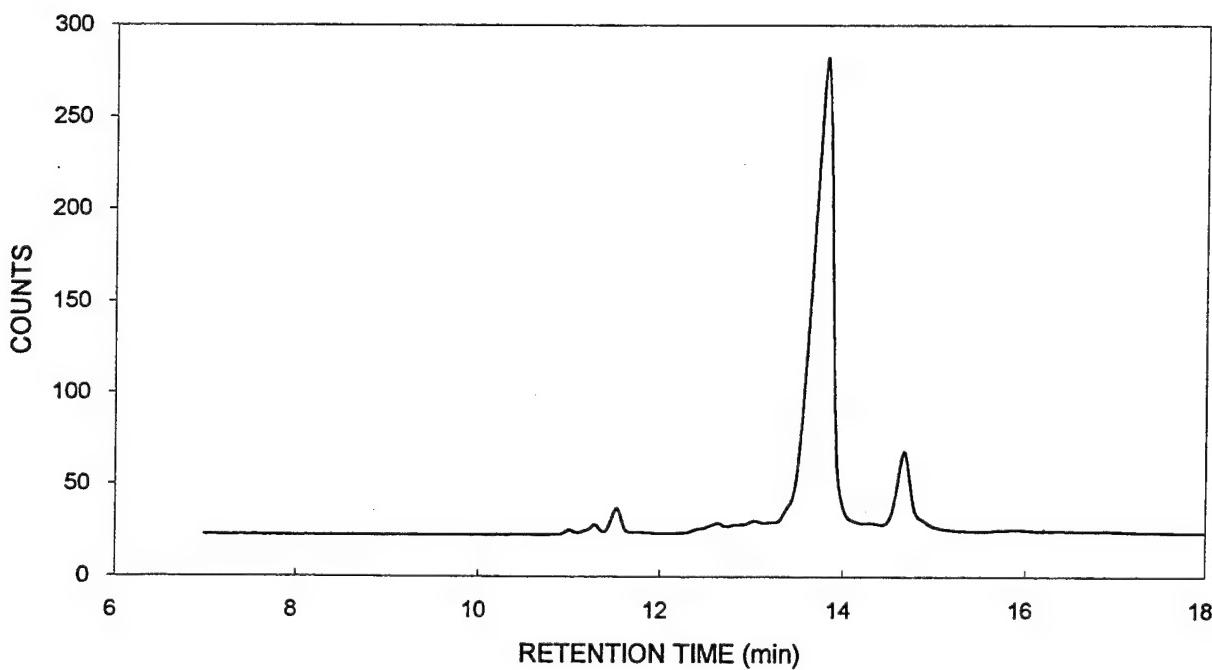


Figure 2. SFC results from unformulated Pennzane 2000.

times cannot be directly compared to those of the phosphate esters to determine vapor pressures, it is clear that the Pennzane features have much longer retention times than the esters, which is consistent with the very low vapor pressure of the base fluid relative to the additives.

Figure 3 provides graphs of the average evaporative losses of four of the materials studied as a function of time and temperature in the volatility test chamber. Data are provided for the neat Pennzane oil, the natural TXP additive, the synthetic FMC 620B, and the synthetic Nye 8478. The data are divided into the four temperature ranges studied, room temperature, 40°C, 55°C, and 65°C, and are presented as a function of time. The same samples were used for all temperatures, thus the weight loss at any given time and temperature is the cumulative loss from the previous time and temperature history of the sample.

There was a wide variation in the volatility of the materials presented in Figure 3. Pennzane showed essentially no weight loss during the nearly 1000 h of testing, consistent with its very low vapor pressure. All of the additives tested, however, showed significant losses. The greatest weight loss was exhibited by the Nye 8478 mixture, due primarily to its very large concentration of the tri-phenyl phosphate component. The SFC data show that this additive contained at least

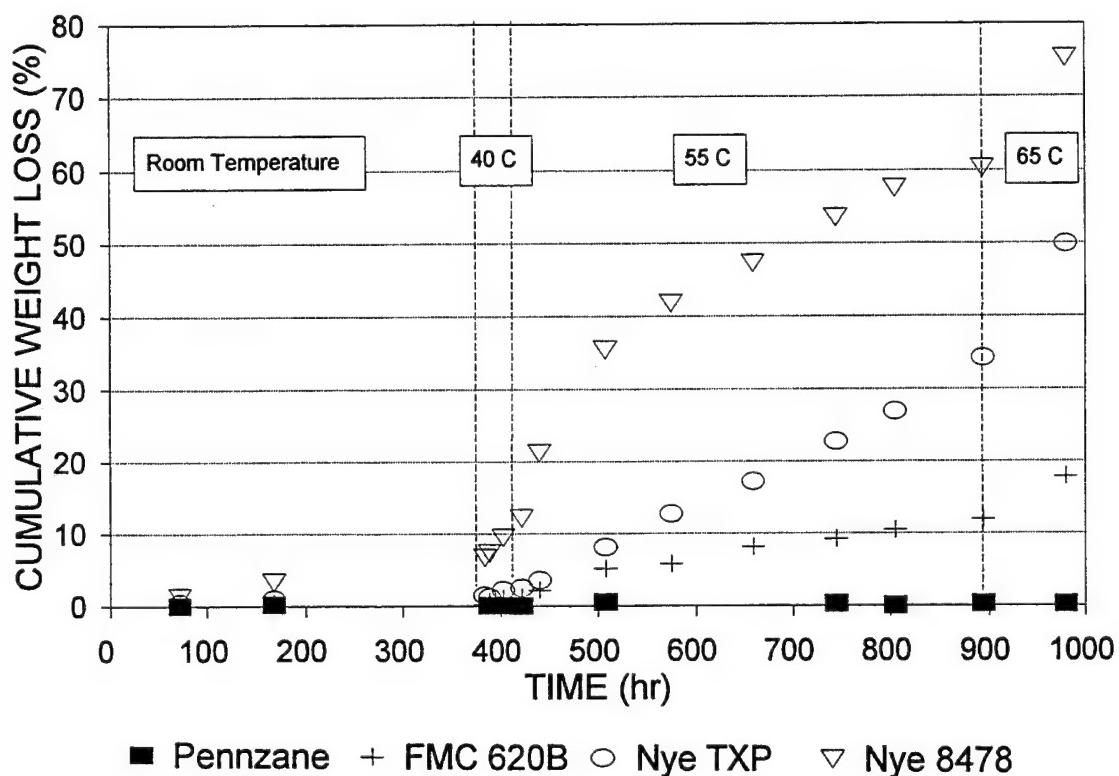


Figure 3. Weight loss results from the evaporation studies of Pennzane, FMC 620B, Nye TXP, and Nye 8478. The average cumulative weight loss for the four materials is provided as a function of time and temperature. The time intervals spent at a particular temperature are marked by the vertical lines, and the temperature is provided on the chart.

30–35% TPP, and the weight loss rate of this mixture was very high until 30–40% of the sample had evaporated. At the higher temperatures examined, this additive has lost 60–75% of its original mass. In contrast to this result are the data for the FMC 620B mixture, which proved this additive to be much less volatile (losing less than 20% of its weight throughout the entire test), consistent with its greater concentration of higher molecular weight species, as seen in Figure 1.

In Figure 3, the TXP compound showed intermediate volatility, as would be predicted from the SFC results. If the experiments were carried on further, however, one would predict that all of the TXP additive would be lost before all of the Nye 8478 because of the significant contributions of the di- and tri-t-butylphenyl compounds in the synthetic additive. Indeed, the slope of the weight loss graph is higher for the TXP mixture than for either of the synthetics near the conclusion of the data acquisition. If data for TCP were presented, one would expect it to be similar to the TXP at the shorter time/lower temperature points, but to have a greater slope than the TXP at longer times, and perhaps intersect the Nye 8478 data trace on this graph.

The conclusion from the evaporation studies is that the volatility of phosphate esters can clearly be controlled by altering their structure. The SFC traces provide an excellent and convenient technique to measure this volatility through the retention time of the major components of the mixture. All of the additives examined in this work are much more volatile than Pennzane, but it is clear that the synthetic phosphate esters can offer a significant improvement if the proper mixture of components is chosen. The question that remains to be addressed is the relative effectiveness of these additives in Pennzane, and this topic will be discussed in the remainder of this report.

3.2 Bearing Test Results

The results of eccentric bearing tests of lubrication conditions A through G (Table 2) are presented in Figure 4. In Figure 4, the average life for a test condition is given by the line separating the two cross-hatched portions of each bar, and the cross-hatched areas represent \pm one standard deviation from the mean value. Starting at the far left of the figure, the performance of neat TCP and neat Pennzane are documented. Under these test conditions, the base oil provides approximately an order of magnitude longer life than the neat TCP, but the remaining tests clearly show the synergism of formulating the oil and additive together. The next two bars show the results obtained from Nye 2001 (Pennzane formulated with a proprietary phosphate ester) and from our formulations of Pennzane with the Nye TXP. These test conditions provided very similar results with average wear lives of ~1.5 million revolutions. One might conclude from these data that Nye is formulating their 2001 lubricant with TXP; however, the SFC traces provided in Figure 5 compare data obtained from neat Pennzane to the 2001 formulation. The data in Figure 5 show only the region of the SFC traces where the additive species appear (i.e., 7 to 10 min). It is clear from these data that the 2001 contains a synthetic additive mixture with species similar to those in the synthetic additives discussed earlier (see Figure 1).

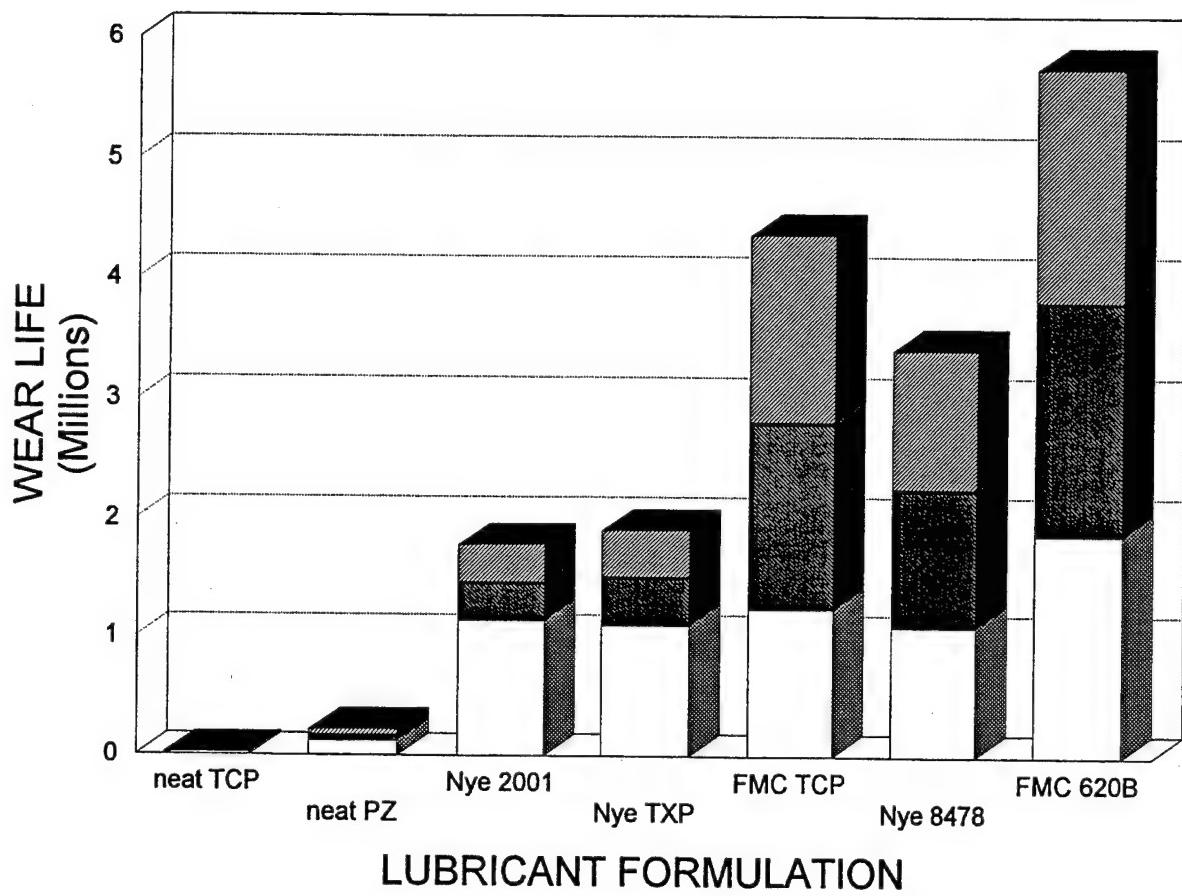


Figure 4. Wear test endurance results for test conditions A through G (Table 2). The average life for each condition is the dividing line between the cross-hatched areas of each bar. The cross-hatched regions represent one standard deviation from the mean.

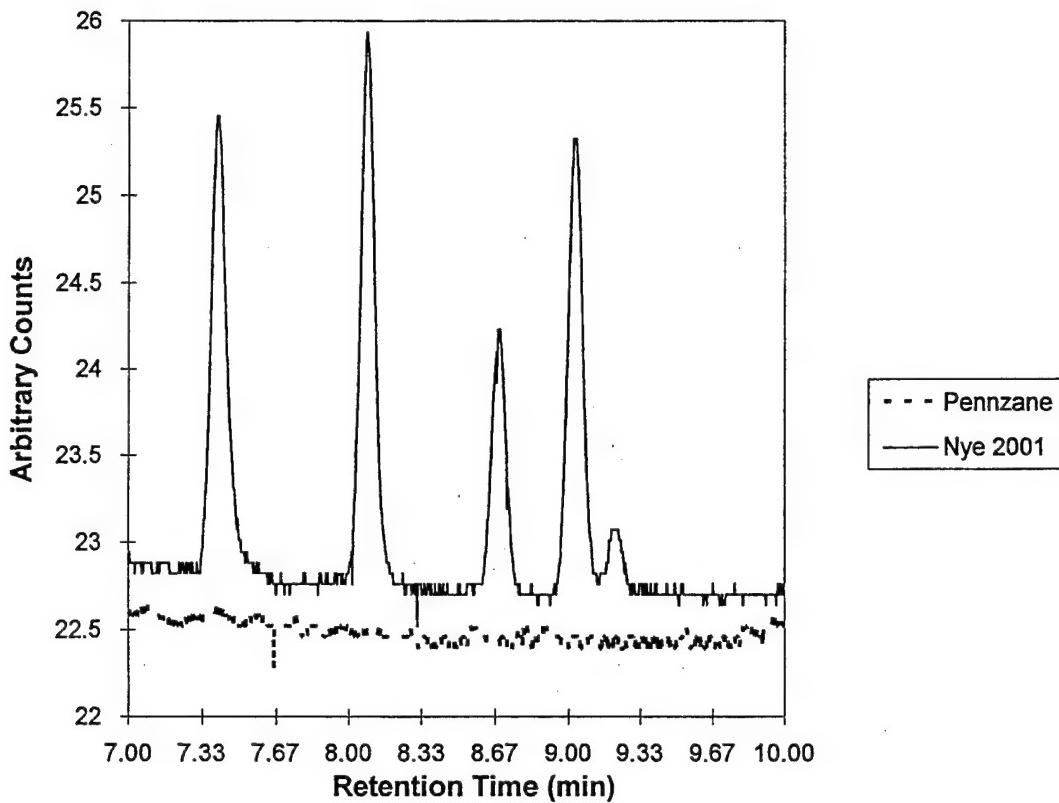


Figure 5. SFC traces showing the additive containing region for unformulated Pennzane and the commercially formulated Nye 2001. Compare the Nye 2001 results to the additive results from Figure 1.

The fifth column in Figure 4 provides the results from Pennzane formulated with FMC TCP. This interesting result shows that this additive lasted approximately two times longer than the tests done with the Nye TXP. There was a much greater spread in the TCP results, leading to the large standard deviation and prompting us to run more tests with this combination than any other. The TCP results are also surprising in comparison to the results obtained with the synthetic additives, provided by the final two bars in Figure 4. The Nye 8478 outperformed the Nye TXP, but had a shorter average life than the TCP. Alternatively, the FMC 620B had the best overall performance, averaging nearly four million revolutions, although the large standard deviations for the final three test conditions indicate that more testing should be done.

The relative performance of the two synthetic additives is logical based on the volatility results presented earlier in this report. The FMC 620B had much lower evaporation rates than any of the other additives tested, and its better performance is probably due, in large part, to its lower volatility, resulting in a higher concentration of additive species during the tests. In addition, the two synthetic additives are composed of similar materials, making possible structural effects on additive performance less important in a comparison of these materials. The tests conducted in this work ran at fairly high temperatures, equilibrating in the range of 70–90°C. The evaporation results presented earlier show that all of the additives are quite volatile in this temperature range, but the FMC 620B is clearly the least volatile. At the speeds used in these tests, it takes about

9.25 h to accumulate 1 million revolutions. It is clear that many of the additives would experience significant evaporation under these temperature and time conditions. However, the fact that the results from all of the additives don't precisely mirror the volatility trends indicates that other factors play a role in determining the performance of the phosphate esters. Among the possibilities, changes in the molecular structure may cause some molecules to be more effective than others. Our lack of understanding regarding the mechanism of the chemical reactivity of these materials in the mechanical contact hinders any further interpretation of these data.

The presence of impurities in the additives could also have impacted the test performance results. In particular, the presence of acidic species in the additives is a potential concern, and the manufacturers' analyses are provided in Table 1. In comparing the two natural additives, the Nye TXP was approximately twice as acidic as the FMC TCP. The same can be said of the Nye 8478 relative to the FMC 620B. In each case, the FMC product outperformed the Nye material in our testing. It is possible, therefore, that several factors control the performance of the phosphate esters, including structure, volatility, and impurity concentration.

3.3 Modified Wear Tests

In virtually all space applications, components to be lubricated with phosphate ester-containing oils are also pretreated with the additive to form an initial protective coating. There has been much debate about the relative value of this pretreatment and the chemical nature of the films that it creates, and we have performed some bearing tests to address these issues. In Figure 6, the test results from several different test conditions are grouped. Included on this chart are test conditions A, B, D, H, and J (see Table 2). Test results A, B, and D were shown in Figure 4, and are the results from neat TCP, neat Pennzane, and Pennzane formulated with the Nye TXP. Test condition H provides the results from test components that were pretreated with TCP, but then lubricated and tested with unformulated oil. It is evident that the pretreatment provides some benefit since the tests ran approximately twice as long as unformulated Pennzane with no pretreatment (condition B), but the beneficial effect was much less than that obtained with the additive formulated in the oil (condition D; even greater life was demonstrated with TCP formulated Pennzane).

Test condition J provides some very important information. This test was started with TXP-formulated oil without any component pretreatment, run for 180,000 revolutions, and then stopped. The test components were then cleaned ultrasonically with heptane to remove free oil and additive, and then the bearing was re-lubricated with unformulated Pennzane and run to failure. The resulting wear life of the condition J test was nearly as long as those run to failure with the TXP-formulated oil, and clearly much longer than pretreated bearing components tested with unformulated Pennzane. Even though only one test was performed under these conditions, it lasted more than twice as long as any single test performed with unformulated oil and pretreated parts. This single test provides strong evidence that the protective film formed during bearing operation with formulated oils is much more effective in extending the life of Pennzane-lubricated systems than mere pretreatment of the bearing components. The remaining question is whether there is any benefit to having both the pretreatment and formulated oil in a lubricated mechanism.

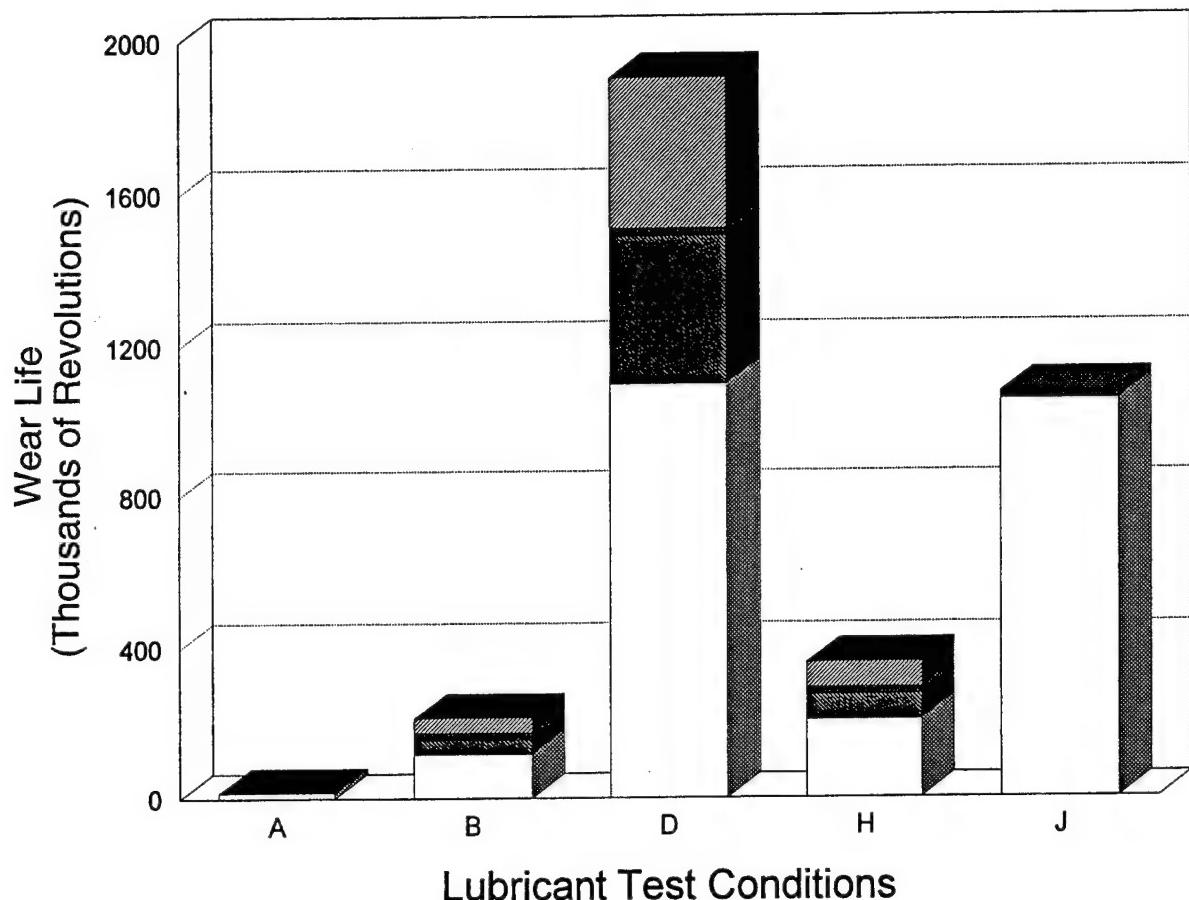


Figure 6. Wear test results from test conditions A, B, D, H, and J. These tests show the relative value of pretreating bearing components (H) as compared to running a bearing with formulated oil (D and J). See text for details.

Figure 7 compares the results from conditions D, G, and H to those from condition I, where the test components were pretreated with TCP and then run with either TXP- or FMC 620B-formulated Pennzane. These results show a tremendous benefit in using pretreated components with formulated oil relative to testing with either condition by itself. Comparable results were obtained with either TXP or 620B-formulated oil, with at least a threefold enhancement of life over tests run with the same lubricants without pretreatment. It must be noted that other tests using a formulated mineral oil and similar lubrication practices did not show this great life enhancement with pretreatment.⁸ Specifically, in those tests, endurance results were virtually identical with TCP-formulated oil with and without the pretreatment. The reasons for these different results are not known, but the test conditions were different in the two studies, with the test articles actively cooled, greater initial lubricant charges, and better lubricant retention in the bearings for the mineral oil tests. One result of the higher temperatures generated in the tests reported here is the more rapid evaporative loss of the additive, possibly enabling the pretreatment to play a greater role than in the controlled-temperature tests. The effect merits further study.

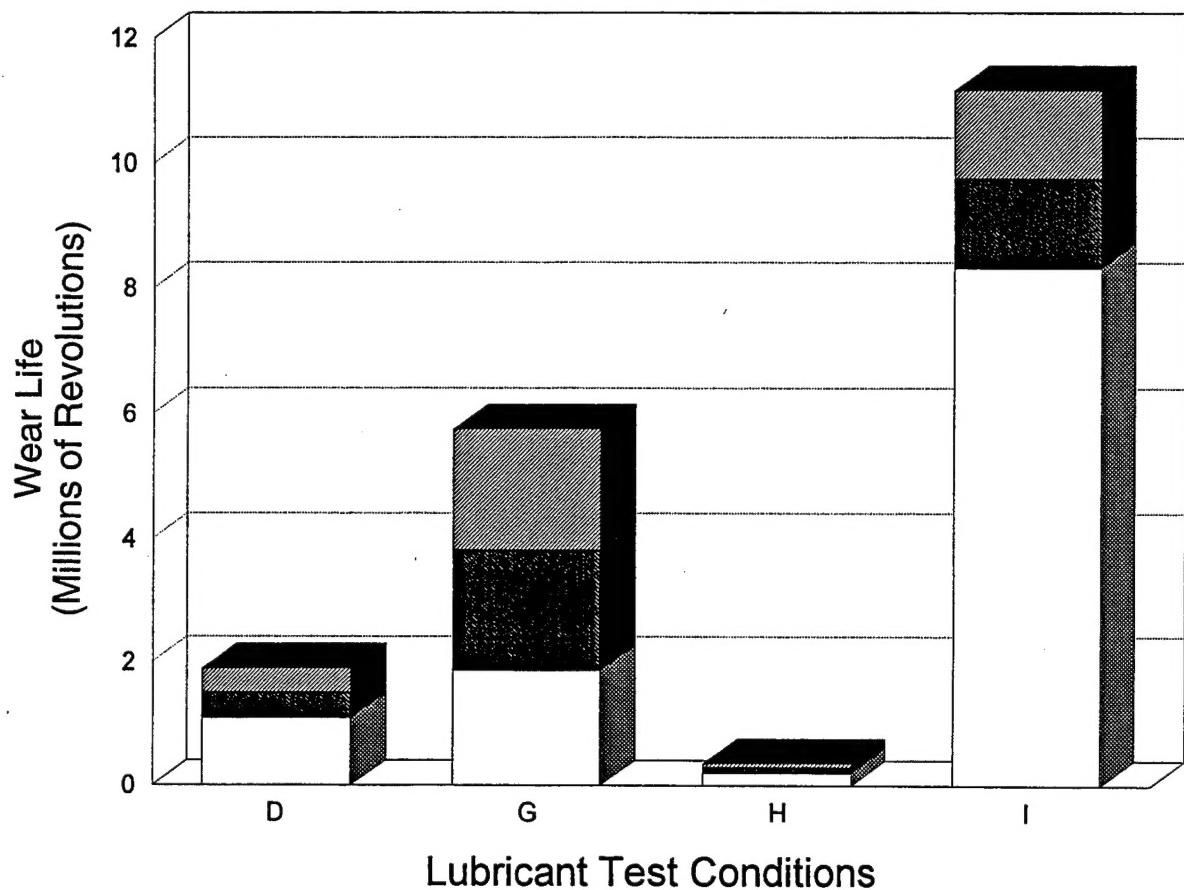


Figure 7. Wear test results comparing test conditions D, G, H, and I. The results from condition I show the benefits obtained from using pre-treated components with formulated oil, versus using only formulated oil (D and G) or pretreated parts with unformulated oil (H).

4. Conclusions

These volatility and bearing performance tests of several commercially available phosphate ester lubricant additives have provided some important initial results. They have clearly demonstrated that the volatility of the additive can be controlled by chemically altering the phenyl rings to increase the molecular weight. Furthermore, the use of SFC to document the distribution of the species present and the resulting effect on material volatility is a powerful and convenient method to study these materials.

The performance tests of the various additive formulations have shown that significant variations in performance exist among the materials tested. In assessing the effect of volatility on additive performance, it can be stated that the least volatile additive examined, the FMC 620B, provided the longest endurance of any of the formulations tested. Using the mean endurance values, the performance of the additives was FMC 620B > FMC TCP > Nye 8478 > Nye TXP. However, the performance of the additives did not precisely follow the expected trend based solely on volatility. From the evaporation experiments and the SFC results, one would expect the initial volatility (up to 50% weight loss) to be FMC 620B < Nye TXP ≤ FMC TCP < Nye 8478. If one was concerned with the final volatility (50–100% weight loss), then the SFC data would predict FMC 620B < Nye 8478 < Nye TXP < FMC TCP. In comparing this series to the performance data, the FMC TCP clearly stands out as breaking the trend. It is possible that structural effects and impurities may play a role in the relative effectiveness of the materials. It is also quite clear from the pretreatment and run-in tests of the additives that an effective anti-wear film can be established quite early with formulated oil under the aggressive test conditions used in this study. This result may indicate that the volatility plays a secondary role for these tests, and that long-term, less severe conditions are necessary for volatility effects to be truly tested in this type of study.

References

- 1 C. G. Vernier, E. W. Casserly, and S. Gunsel, "Tris(2-Octyldodecyl)Cyclopentane, a Low Volatility, Wide Liquid Range, Hydrocarbon Fluid," *J. Syn. Lub.* **9** (1992) 237.
- 2 D. J. Carré, C. G. Kalogeras, S. V. Didziulis, P. D. Fleischauer, and R. Bauer, "Recent Experiences with Synthetic Hydrocarbon Lubricants," *Proceedings of the Sixth European Space Mechanisms and Tribology Symposium*, 4–6 October 1995, European Space Agency, Paris (1995).
- 3 P. A. Bertrand and D. J. Carré, "The Vapor Pressure of Lead Naphthenate," TOR-93(3478)-3, The Aerospace Corporation, El Segundo, CA, 1 June 1993.
- 4 S. V. Didziulis and P. D. Fleischauer, "The Chemistry of the Extreme Pressure Lubricant Additive Lead Naphthenate on Steel Surfaces," *Langmuir* **7** (1991) 2981.
- 5 M. R. Hilton, C. G. Kalogeras, and S. V. Didziulis, "Investigation of Multiply Alkylated Cyclopentane Synthetic Oil and Lead Naphthenate Additive under Boundary Contact Interactions," ATR- 93(8361)-1, The Aerospace Corporation, El Segundo, CA, 1 September 1992.
- 6 C. Kalogeras, M. Hilton, D. Carré, S. Didziulis, and P. Fleischauer, "The Use of Screening Tests in Spacecraft Lubricant Evaluation," *Proc. 27th Aerospace Mechanisms Symposium*, 12–14 May 1993, NASA Conf. Pub. 3205, p. 197.
- 7 M. P. Marino and D. G. Placek, "Phosphate Esters," in *Handbook of Lubrication and Tribology*, Vol. III, R. E. Booser, ed., CRC Press, Boca Raton, FL, 1994, pp. 269–286. Recent unpublished work by Carré and Bertrand has shown the vapor pressure to be lower than published estimates of 10^{-5} to 10^{-6} Torr.
- 8 C. G. Kalogeras and S. V. Didziulis, "Bearing Tests of Lubricant Additive Formulation and Pretreatment Processes," TR-95(5935)-5, The Aerospace Corporation, El Segundo, CA, 20 December 1995.

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